EP0311678;;

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.R<sup>10</sup>

R<sup>11</sup>

R<sup>10</sup>

k12

R<sup>12</sup>

We claim:

A process for preparing racemic metallocene complexes of the formula (I) 1.

R8.

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15 R8: (1)

20 where

is a divalent group such as

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and

is a divalent group such as

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and the substituents and indices have the following meanings:

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M

is titanium, zirconium or hafnium,

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R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, R<sup>11</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup> are identical or different and are each hydrogen, halogen, C<sub>1</sub>–C<sub>20</sub>–alkyl, 3– to 8–membered cycloalkyl which may in turn bear a C<sub>1</sub>–C<sub>10</sub>–alkyl group as substituent, C<sub>6</sub>–C<sub>15</sub>–aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

-OR<sup>13</sup>, -SR<sup>13</sup>, -N(R<sup>13</sup>)<sub>2</sub>, -P(R<sup>13</sup>)<sub>2</sub>, or Si(R<sup>13</sup>)<sub>3</sub>, where are identical or different and are each  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{15}$ -aryl,  $C_3$ - $C_{10}$ -cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully

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R<sup>8</sup>, R<sup>12</sup> are identical or different and are each C<sub>1</sub>-C<sub>10</sub>-alkyl,

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v

R13

are oxygen -O-

substituted by heteroatoms,

 $R^7$  is a -[Z( $R^{15}$ )( $R^{16}$ )]<sub>m</sub>- group, where

Z can be identical or different and are each silicon, germanium, tin or carbon,

R<sup>15</sup>, R<sup>16</sup> are each hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl or C<sub>6</sub>-C<sub>15</sub>-aryl,

m is 1, 2, 3 or 4,

10 by reacting a transition metal complex of the formula (II)

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where

are identical or different and are each hydrogen, halogen, C<sub>1</sub>–C<sub>10</sub>–alkyl, C<sub>6</sub>–C<sub>15</sub>–aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, –OR<sup>17</sup> or -NR<sup>17</sup><sub>2</sub>, where R<sup>17</sup> are identical or different and are each C<sub>1</sub>–C<sub>10</sub>-alkyl, C<sub>5</sub>-C<sub>15</sub>-aryl, C<sub>3</sub>–C<sub>10</sub>-cycloalkyl, alkylaryl,

n is an integer from 1 to 4 and corresponds to the valence of M minus 2,

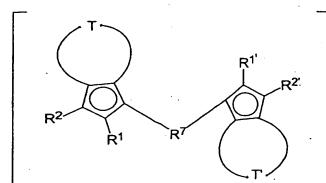
with cyclopentadienyl derivatives of the formula (III)

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where

M<sup>2</sup>

is an alkali metal ion or alkaline earth metal ion,

and

р

is 1 when  $\ensuremath{\text{M}^2}$  is an alkaline earth metal ion and is 2 when  $\ensuremath{\text{M}^2}$  is an alkali metal

р M<sup>2</sup>

ion,

and heating the resulting reaction mixture to a temperature in the range from -78 to +250°C.

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2. A process as claimed in claim 1 for preparing racemic metallocene complexes of the formula (I)

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$$R^{2}$$
 $R^{1}$ 
 $R^{1}$ 
 $R^{12}$ 
 $R^{11}$ 
 $R^{12}$ 
 $R^{11}$ 
 $R^{12}$ 
 $R^{11}$ 

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**(I)** 

where

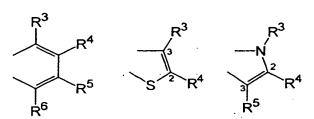
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J

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is a divalent group such as

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and

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is a divalent group such as

10 and the substituents and indices have the following meanings:

M is titanium, zirconium or hafnium,

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>
are identical or different and are each hydrogen, halogen, C<sub>1</sub>–C<sub>20</sub>–alkyl, 3– to 8–membered cycloalkyl which may in turn bear a C<sub>1</sub>–C<sub>10</sub>–alkyl group as substituent, C<sub>6</sub>–C<sub>15</sub>–aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

-OR<sup>13</sup>, -SR<sup>13</sup>, -N(R<sup>13</sup>)<sub>2</sub>, -P(R<sup>13</sup>)<sub>2</sub> or Si(R<sup>13</sup>)<sub>3</sub>, where

are identical or different and are each C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully

 $R^8$ ,  $R^{12}$ ,  $R^{8'}$ ,  $R^{12'}$  are identical or different and are each  $C_1$ - $C_{10}$ -alkyl,

substituted by heteroatoms,

Y are oxygen -O-

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 $R^7$  is a -[ $Z(R^{15})(R^{16})$ ]<sub>m</sub>- group, where

Z can be identical or different and are each silicon, germanium, tin or carbon,

 $R^{15}$ ,  $R^{16}$  are each hydrogen,  $C_1$ - $C_{10}$ -alkyl,  $C_3$ - $C_{10}$ -cycloalkyl or  $C_6$ - $C_{15}$ -aryl,

m is 1, 2, 3 or 4,

10 comprising the following steps:

a) deprotonation of a compound of the formula (IV)

$$R^2$$
 $T$ 
 $T$ 
 $T$ 
 $R^2$ 
 $R^2$ 
 $R^3$ 

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by means of a suitable deprotonating agent;

b) reaction of the deprotonated compound (IV) with a compound R<sup>7</sup>Hal<sub>2</sub>, where Hal is a halogen substituent such as F, Cl, Br or I, and subsequent repeat deprotonation by means of a suitable deprotonating agent to give the compound of the formula (III)

 $p M^2$ 

(III)

where

 $M^2$ 

р

is an alkali metal ion or alkaline earth metal ion,

where

is 1 when M2 is an alkaline earth metal ion and is 2 when M2 is an alkali metal ion, and R7 is as defined above;

b)

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reaction of the compound of the formula (III) with a transition metal complex of the formula (II)

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(11)

where

Х are identical or different and are each hydrogen, halogen, C1-C10-alkyl, C6-C<sub>15</sub>-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, -OR17 or-NR172, where R17 are identical

to 20 carbon atoms in the aryl part,  $-OR^{17}$  or- $NR^{17}_{21}$ , where  $R^{17}$  are identical or different and are each  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{15}$ -aryl,  $C_3$ - $C_{10}$ -cycloalkyl, alkylaryl, is an integer from 1 to 4 and corresponds to the valence of M minus 2, and the other substituents are as defined above.

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n

## 3. A racemic metallocene complex of the formula (I)

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$$R^{2}$$
 $R^{1}$ 
 $R^{1}$ 
 $R^{1}$ 
 $R^{12}$ 
 $R^{11}$ 
 $R^{12}$ 
 $R^{11}$ 
 $R^{12}$ 
 $R^{11}$ 
 $R^{10}$ 

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where

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**(I)** 

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is a divalent group such as

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and



is a divalent group such as

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and the substituents and indices have the following meanings:

M

is titanium, zirconium or hafnium,

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R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup> are identical or different and are each hydrogen, halogen, C<sub>1</sub>–C<sub>20</sub>–alkyl, 3– to 8–membered cycloalkyl which may in turn bear a C<sub>1</sub>–C<sub>10</sub>–alkyl group as substituent, C<sub>6</sub>–C<sub>15</sub>–aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, -OR<sup>13</sup>, -SR<sup>13</sup>, -N(R<sup>13</sup>)<sub>2</sub>, -P(R<sup>13</sup>)<sub>2</sub> or Si(R<sup>13</sup>)<sub>3</sub>, where

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R<sup>13</sup> are identical or different and are each C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully substituted by heteroatoms,

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 $R^8$ ,  $R^{12}$ ,  $R^8$ ,  $R^{12}$  are identical or different and are each  $C_1$ - $C_{10}$ -alkyl,

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are oxygen -O-



5	R <sup>7</sup>	is a - $[Z(R^{15})(R^{16})]_{m}$ - group, where
	z	can be identical or different and are each silicon, germanium, tin or carbon,
	R <sup>15</sup> , R <sup>16</sup> and	are each hydrogen, $C_1$ - $C_{10}$ -alkyl, $C_3$ - $C_{10}$ -cycloalkyl or $C_6$ - $C_{15}$ -aryl,
	m	is 1, 2, 3 or 4.

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A process or complex as claimed in any of the preceding claims, wherein the substituents R<sup>8</sup>, R<sup>8'</sup> and R<sup>12</sup>, R<sup>12'</sup> are identical and are selected from among methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl and tert-butyl, particularly preferably methyl.

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A process or complex as claimed in any of the preceding claims,
 wherein the substituents R¹ and R¹ are identical or different and are each hydrogen or methyl.

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A process as claimed in claim 9,

- 6. A process or complex as claimed in any of the preceding claims, wherein M is zirconium.
- 5 7. A process or complex as claimed in any of the preceding claims, wherein M<sup>2</sup> is magnesium or lithium.
  - 8. A process or complex as claimed in any of the preceding claims, wherein R<sup>7</sup> is a dimethylsilyl group or an ethanediyl group.

A process as claimed in any of claims 1, 2 and 4 to 8,
 wherein, in a further step, the compound of the formula (I) is reacted with suitable replacement reagents to replace at least one of the groups

by halogen substituents such as F, Cl, Br or I or by linear, branched or cyclic  $C_{1-10}$ -alkyl substituents.

wherein the replacement reagents are selected from among aliphatic and aromatic carboxylic acid halides such as acetyl chloride, phenylacetyl chloride, 2—thiophenacetyl chloride, trichloroacetyl chloride, trimethylacetyl chloride, O—acetylmandelyl chloride, 1,3,5—benzenetricarboxylic chloride, 2,6—pyridinecarboxylic chloride, tert—butylacetyl chloride, chloroacetyl chloride, 4—chlorobenzacetyl chloride, dichloroacetyl chloride, 3—methoxyphenylacetyl chloride, acetyl bromide, bromoacetyl bromide, acetyl fluoride, benzoyl fluoride, SOCl<sub>2</sub>, silicon tetrachloride, organoaluminum compounds such as tri-C<sub>1</sub>-C<sub>10</sub>-alkylaluminums, in particular trimethylaluminum, triethylaluminum, tri-n-butylaluminum, triisobutylaluminum, and dialkylaluminum chlorides, aluminum sesquichlorides, methylaluminum dichloride and combinations thereof.

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- A process as claimed in claim 9, 11. wherein replacement reagents used are HF, HBr, HI, preferably HCI, as such or as solutions in water or organic solvents such as diethyl ether, DME or THF.
- 12. A process as claimed in any of claims 1, 2 and 4 to 11, wherein the deprotonating agent is selected from among n-butyllithium, tert-butyllithium, sodium hydride, potassium tert-butoxide, Grignard reagents of magnesium, magnesium compounds such as, in particular, di-n-butylmagnesium, (n,s)-dibutylmagnesium and other suitable alkaline earth metal alkyl and alkali metal alkyl compounds.
- A process as claimed in any of claims 1, 2 and 4 to 12, wherein no intermediates are isolated during the process.
- 15 A complex as claimed in claim 3 selected from among dimethylsilylbis(1-indenyl)zirconium 14. bis(2,4,6-trimethylphenoxide), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,4,6trimethylphenoxide), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,6dimethylphenoxide), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,6-dimethyl-4bromophenoxide) and ethanediylbis(1-indenyl)zirconium bis(2,4,6-trimethylphenoxide).
  - The use of a racemic metallocene complex as claimed in any of claims 3 to 8 and 14 as a 15. catalyst or as a constituent of a catalyst for the polymerization of olefinically unsaturated compounds or as a reagent or catalyst in stereoselective synthesis.

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